



Conversion of biomass to γ -valerolactone by catalytic transfer hydrogenation of ethyl levulinate over metal hydroxides

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ABSTRACT

A series of low-cost readily-assembled eco-friendly metal hydroxides were examined as catalysts in the synthesis of a novel platform molecule, γ -valerolactone (GVL), from biomass-derived ethyl levulinate (EL) via hydrogen transfer reaction. Among these catalysts, $\text{ZrO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ was found to be most active. EL conversion of 93.6% and GVL selectivity of 94.5% were achieved when 2-propanol was used as a hydrogen donor at 473 K with a reaction time of only 1 h. The complete reaction pathway and the probable main by-products for the conversion of EL to GVL were clearly deduced for the first time. The $\text{ZrO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ catalyst could be reused at least ten times without any significant loss of catalytic activity. Furthermore, characterizations were carried out on the fresh and spent $\text{ZrO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ catalysts with XRD, FT-IR, BET, TGA-DTA. Combined with the results of poisoning experiments, a plausible mechanism for catalytic transfer hydrogenation (CTH) of EL to GVL was proposed to be consisted of a catalytic cycle involving a six member ring transition state.

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1. Introduction

Depletion of fossil-based resources and deterioration of environmental have raised the concerns on the sustainability of our society, economy and environment. In recent decades, various renewable resources were studied and developed in order to meet the growing energy demands. Among them, abundant and inexpensive biomass is the only renewable resources on the earth that can be converted to liquid fuels and chemicals which are conventionally derived from fossil resources [1,2]. The transformation of biomass to platform molecules, the precursor for the synthesis of a substantial number of value-added chemicals and transportation fuels, has attracted increasing attention of researchers worldwide [2–6]. In recent years, a variety of catalytic strategies have been developed for the generation of platform chemicals, including 5-hydroxymethylfurfural (HMF) [7–10], levulinic acid (LA) [11,12] and γ -valerolactone (GVL) [13,14], which can be readily derived from carbohydrates or even directly from biomass. GVL is identified as a versatile building block that can be applied to produce various value-added chemicals which are well-suited as organic solvents and bio-oxygenates [15,16]. Moreover, GVL can also be used to synthesize various liquid hydrocarbons with a suitable

molecular weight to meet the qualities for gasoline, diesel and aviation kerosene [17–19], respectively. GVL itself has also been described as an excellent green solvent in biomass conversion, which resulted in a higher yield and effective separation of desired products from biomass due to its outstanding physicochemical properties [20–23].

GVL is usually produced through selective reduction of biomass-derived LA under high-pressure H_2 in homogeneous and/or heterogeneous systems [24,25]. Until now, a variety of catalytic systems have been developed for the production of GVL from LA, and Ru-based catalysts were confirmed as most active [26–28]. However, the drawbacks of being high cost, prone to deactivation and difficult to regenerate limited the applications of noble metal catalysts in a commercial scale GVL production. Moreover, there are safety concerns on the use of corrosive LA and hazardous H_2 . For instance, the cost of transportation and storage of hydrogen are probably more expensive than the biomass feedstock itself [29]. A cost-efficient separation and purification process of LA from biomass seems impossible due to its high acidity and low volatility. Thus, EL, which can also be derived from biomass via ethanolysis [30,31], is a better alternative than LA for the production of GVL as EL is acid-free and easy-separable [32,33]. However, a poor performance was observed for the selective hydrogenation of levulinate esters under high-pressure H_2 [34,35]. Therefore, it is important to develop a new catalytic process for the production of GVL from EL.

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Recently, Yao Fu's group was reported an effective catalytic transfer hydrogenation (CTH) route to convert biomass-derived EL to GVL over Raney Ni under room temperature [36]. Differing from the CTH route employed by Yao Fu, the CTH of carbonyl compounds via Meerwein–Ponndorf–Verley (MPV) reduction was extensively studied in the organic synthesis [37]. Carbonyl compounds can be converted to their corresponding alcohols by MPV reduction with a high selectivity over low-cost metal oxides [38]. Using abundant and safe alcohols as hydrogen donor is another unique advantage for the MPV reduction of carbonyl compounds. Although high yields of the desired alcohols were obtained when this CTH approach was applied to an open system through a solvent refluxing method, an extended reaction time (longer than dozens of hours) was essential [39]. Nevertheless, MPV reaction in a sealed reactor under high temperature and saturated pressure was rarely studied, especially for the reduction of biomass-derived EL to GVL [40]. Recently, our group has reported the CTH of EL to GVL over metal oxides [41]. In this work, we discovered that metal hydroxides were more effective than metal oxides for the CTH of EL. Herein, an effective and green process was developed for the conversion of biomass-based EL to GVL via MPV reduction in various subcritical alcohols over the low-cost eco-friendly metal hydroxides. The effects of varied experiment parameters on the selectivity of products were systematically investigated and a detailed characterization of the fresh and used catalysts was conducted. Finally, based on the results of the poisoning experiments, a plausible mechanism for the CTH of levulinate esters to GVL via MPV reduction over metal hydroxides was proposed.

2. Experimental procedure

2.1. Chemicals and materials

EL (98%), GVL (98%) and zirconium oxychloride (99%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Butyl levulinate (BL) and methyl levulinate (ML) were obtained from Alfa Aesar Co. Ltd. (Tianjin, China). All other chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification.

2.2. Catalysts preparation

All metal hydroxides were prepared by precipitation using their chloride salts as the precursors. In a typical procedure, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in deionized water to prepare a 100 g/L $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution. Concentrated NH_4OH was added to adjust the solution pH value around 9.5 with vigorous stirring, and then the resulting emulsion was aged at room temperature for 24 h before separating the white precipitate. The precipitate was thoroughly washed with deionized water until the chloride ions could not be identified in the filtrate. The washed precipitate was dried at 383 K for 12 h, and then was ground to pass a 100-mesh sieve.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on a Panalytical X'pert Pro diffractometer using a $\text{Cu K}\alpha$ radiation source with the following parameters: 40 kV, 30 mA, 2θ from 20° to 90° at a scanning speed of $7^\circ/\text{min}$. FT-IR spectrums were recorded on a Nicolet 380 spectrometer. SEM images were performed on a Hitachi S-4800 by using 30 kV. Thermal gravimetric analysis and differential thermal gravimetric analysis (TGA/DTG) were carried out on a SDT Q600 thermal analyzer under a dynamic N_2 atmosphere (100 mL/min) at the temperature range of 293–1173 K with a heating rate of 20 K/min. BET surface areas were measured on a TriStar 3000 surface area and porosimetry analyzer (Micromeritics), the samples

were degassed at 373 K for 3 h in a vacuum before N_2 adsorption. Elemental analyses were performed by an Elementar Vario EL III (Elementar Analysensysteme GmbH, Germany).

2.4. Typical procedure for the production of GVL

The experiments were carried out in a 100 mL cylindrical stainless steel high-pressure reactor (PARR instrument company, USA). In a typical reaction, the batch autoclave reactor was loaded with substrate (2 g), solvent (38 g) and catalyst (1 g), and then purged five times with N_2 at atmospheric conditions before the reaction mixture was heated to the prescribed temperature for a desired reaction time with stirring at 500 rpm. After reaction, the reactor was cooled to room temperature. The liquid products were centrifuged at 10,000 rpm for 5 min and analyzed by GC–MS and GC methods, respectively.

2.5. Sample analysis

The qualitative analysis of sample after reaction was conducted with a Shimadzu QP2010SE instrument with Rtx-5MS column ($30.0 \text{ m} \times 0.25 \mu\text{m} \times 0.25 \text{ mm}$) and electron impact ionization (EI).

The amount of levulinate esters and its products were determined on an Agilent 7890 series equipped with a HP-5 capillary column ($30.0 \text{ m} \times 320 \mu\text{m} \times 0.25 \mu\text{m}$) and a flame ionization detector (FID) operating at 543 K. The carrier gas was N_2 with a flow rate of 1.0 mL/min. The following programmed temperature was used in the analysis: 313 K (4 min) – 15 K/min – 623 K (5 min). Typically, EL conversion, GVL yield, GVL selectivity and GVL formation rate were calculated using the following equations:

$$\text{EL conversion (\%)} = \left(1 - \frac{\text{Mole of EL}}{\text{Initial mole of EL}} \right) \times 100\% \quad (1)$$

$$\text{GLV yield (\%)} = \frac{\text{Mole of GLV}}{\text{Initial mole of EL}} \times 100\% \quad (2)$$

$$\text{GLV selectivity (\%)} = \frac{\text{Mole of GLV}}{\text{Initial mole of EL} - \text{Mole of EL}} \times 100\% \quad (3)$$

$$\text{GLV formation rate } (\mu\text{mol/g/min}) = \frac{\text{Mole of GLV}}{\text{Amount of catalyst} \times \text{Reaction time}} \quad (4)$$

3. Results and discussion

3.1. Evaluation and screening of catalyst

To the best of our knowledge, the CTH of biomass-derived EL to GVL over inexpensive metal hydroxides has not been reported prior to this paper. As shown in Table 1, the catalytic activities of various metal hydroxides for the CTH of EL to GVL were largely different when ethanol was used as a hydrogen donor. The reaction mixture consisted of 2 g EL and metal hydroxide in 38 g ethanol. The reactor was heated to 473 K for 60 min. $\text{Zr}(\text{OH})_4$ produced the most GVL yield with an EL conversion of 50.9% and a GVL yield of 43.1% (Table 1, entry 8). However, when $\text{La}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ were used as catalysts, EL conversions were no greater than 25% (Table 1, entries 5–7). Moreover, GVL yields were negligible in the presence of $\text{Cr}(\text{OH})_3$, $\text{Sn}(\text{OH})_4$ and $\text{Ni}(\text{OH})_2$ probably due to their weak basicity (Table 1, entries 1–3). It is noticeable that EL was mostly converted in the presence of strong Bronsted bases. EL conversion of 100% was reached when NaOH was employed as the catalyst, but considerable coke, rather than GVL, was observed under the above-mentioned reaction conditions. This observation might be attributed to that condensation reactions of EL increased

Table 1
CTH of EL to GVL catalyzed by various metal hydroxides.^a

Entry	Catalyst ^b	Conversion (%)	Yield (%)
1	Cr(OH) ₃	6.0	1.3
2	Sn(OH) ₄	13.5	1.5
3	Ni(OH) ₂	3.0	1.1
4	Fe(OH) ₃	12.6	7.2
5	Mg(OH) ₂	11.4	4.7
6	Al(OH) ₃	9.9	5.2
7	La(OH) ₃	24.9	14.6
8	Zr(OH) ₄	50.9	43.1
9	Ca(OH) ₂	54.6	14.5
10	Ba(OH) ₂	91.5	8.2
11	NaOH	100.0	0.0

^a Reaction conditions: 2 g EL, 38 g ethanol, 473 K, 60 min, 500 rpm, N₂ at atmospheric conditions.

^b Metal hydroxides with equimolar quantities of hydroxyl were used as the catalysts. For instance, 0.0063 mol (1 g) Zr(OH)₄ containing 0.025 mol hydroxyl were added as the catalyst in entry 8.

at the expense of GVL yield over the strong base. Hence, it is essential to select the catalysts with moderate basicity to ensure a high GVL yield.

3.2. The effects of hydrogen donors

Given the outstanding performance of Zr(OH)₄ for the CTH of EL to GVL, the effects of various hydrogen donors (in place of ethanol) were thoroughly surveyed with Zr(OH)₄ being the catalyst. The activity of hydrogen donors for the CTH of EL relies heavily on the reduction potential (Table S1) of the reducing alcohols used. The reduction potential, $\Delta_f H^\circ$, is defined as the difference of the standard molar enthalpy of formation between the alcohol and the corresponding carbonyl compound; namely, it represents the ease of hydrogen abstraction [37,42]. As shown in Table S1, the reduction potential of reducing alcohols decreased in the order of: 2-propanol \approx 2-butanol < 1-butanol < ethanol < methanol. The reduction potential of methanol is much higher than other alcohols, which resulted in a poor performance as the H-donor (Table 2, entries 1–2). The secondary alcohols (e.g. 2-propanol) have the lowest reduction potential; therefore, they have the best reducing capacities to ensure the highest GVL yields (Table 2, entries 7 and 8).

As can be seen from Table 2, 2-propanol and 2-butanol performed excellently with an EL conversion of 93.6 and 91.9%, respectively (Table 2, entries 7 and 8), followed by ethanol, 1-butanol and methanol (Table 2, entries 1–5). This observation is in line with the reduction potential of the reducing alcohols used (Table S1). It should be noted that transesterification took place when an alcohol other than ethanol was used as the hydrogen donor. For instance, a methyl levulinate (ML) selectivity of 82.2% was observed when the CTH of EL occurred in methanol media

(Table 2, entry 1). As for 1-butanol, only 14.3% butyl levulinate (BL) formed due to the strong steric effects. Both of the CTH of BL to intermediate butyl 4-hydroxypentanoate (4-HPB) and the intramolecular cyclization of 4-HPB to GVL in 1-butanol media are more difficult than the similar conversion of EL in ethanol media, owing to stronger steric effects of BL and 4-HPB than EL and 4-HPE, respectively. For this reasons, the selectivity to GVL from EL or BL in 1-butanol media was lower than that from EL in ethanol media, although 1-butanol has a lower reduction potential than ethanol (Table 2, entries 5–6). Moreover, it is encouraging that a high GVL selectivity with insignificant transesterification was obtained when isopropanol or 2-butanol was utilized as the hydrogen source (Table 2, entries 4 and 6). Obviously, the ketones derived from the secondary alcohols via dehydrogenation are more stable than the aldehydes from the primary alcohols. This result leads us to conclude that fewer side reactions occurred when isopropanol or 2-butanol was used as the hydrogen donor.

3.3. The reaction pathway

Side reactions occurred during the CTH of EL to GVL rendered a GVL selectivity below 100%, even when 2-propanol was used as hydrogen donor (Table 2). To elucidate the reaction pathway, it is crucial to identify the desired product and the main by-products after the reaction. To get more insight into the reaction pathway for the formation of by-products and the effects of varied parameters on the selectivity of products, ethanol was selected as the hydrogen donor for the CTH of EL in the subsequent tests. Ethanol is an appropriate hydrogen source with a relative high EL conversion and an acceptable GVL selectivity. In addition, acetaldehyde formed by the dehydrogenation of ethanol was sufficiently significant to ensure the simultaneous formation of noticeable amount of by-products so that these by-products can be detected easily. Most importantly, it is well-known that EL can be produced directly via alcoholysis of biomass carbohydrates in ethanol media. Based on the economic considerations, the CTH of EL to GVL directly achieved in the ethanol stream from ethanolysis of biomass carbohydrates would be highly desirable. Therefore, the condition experiments conducted with varied parameters in ethanol are very essential for the above-mentioned purpose.

The reaction pathway for the conversion of EL to GVL and by-products in ethanol media was deduced based on the results of GC-MS and shown in Scheme 1. It can be seen that EL gained two hydrogen atoms from ethanol to yield the intermediate ethyl 4-hydroxypentanoate (4-HPE), and then 4-HPE was converted rapidly to either GVL or ethyl 4-ethoxypentanoate (E4EOPA, **1** in Scheme 1) through intramolecular transesterification or etherification with ethanol, respectively. Recently, E4EOPA was produced from GVL and recognized as a promising bio-oxygenate owing to its considerably lower vapor pressure than other oxygenates such as

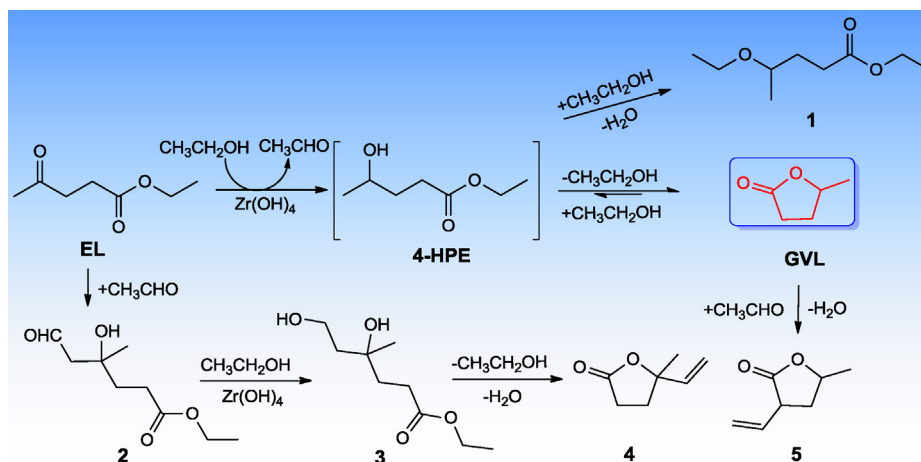
Table 2
Synthesis of GVL from levulinate esters via hydrogen transfer from various alcohols.^a

Entry	Substrate	Solvent	Conversion (%)	Selectivity (%)	
				GVL	Other levulinates
1	EL	Methanol	50.1	12.8	82.2 ML
2	ML	Methanol	13.3	70.7	–
3	EL	Ethanol	50.9	84.6	–
4	EL	<i>tert</i> -Butanol	22.6	16.4	–
5	EL	1-Butanol	60.0	59.5	14.3 BL
6	BL	1-Butanol	44.2	64.9	–
7	EL	2-Butanol	91.9	88.5	Trace SBL ^b
8	EL	2-Propanol	93.6	94.5	Minute amount IPL ^c

^a Reaction conditions: 2 g levulinate esters, 38 g alcohols, 473 K, 1 g Zr(OH)₄, 60 min, 500 rpm, N₂ at atmospheric conditions.

^b SBL means sec-butyl levulinate.

^c IPL means isopropyl levulinate.



Scheme 1. Reaction pathway for the conversion of EL to GVL and by-products.

methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) [15,16]. Moreover, minute amounts of compounds **4** and **5** were also detected by GC-MS, as well as trace amounts of **2** and **3**. It is apparent that the above-mentioned by-products probably formed by aldol condensation between EL, GVL and the aldehyde dehydrogenized from ethanol. However, no detectable 4-HPE was observed by GC-MS analysis. On the one hand, it is suggested that the conversion of 4-HPE to GVL is fast and the hydrogenation of EL to 4-HPE is the rate-limiting step for the conversion of EL to GVL. On the other hand, thermolability of 4-HPE is partially responsible for this observation.[28] Fortunately, 4-HPE was determined clearly by ^1H NMR spectroscopy [16,43]. GC-MS spectra of the products were given in Figs. S1–S5 (supplementary material section).

3.4. EL conversion and the product selectivities

The effect of reaction temperature in the range between 453 and 533 K was shown in Table 3. Elevated temperature promoted EL conversion and GVL formation. An EL conversion of 89.1% and an average GVL formation rate of 179.0 $\mu\text{mol/g/min}$ were achieved when temperature was up to 513 K (Table 3, entry 8). However, the EL conversion and the average GVL formation rate were down to 75.8% and 147 $\mu\text{mol/g/min}$, respectively, when the temperature was further increased to 523 K (Table 3, entry 9). Thus, hydrogen transfer from ethanol to EL was likely suppressed when the temperature exceeded 513 K. The selectivities to GVL and to E4EOPA were maintained at around 82% and 10%; respectively, with little fluctuations. It is noted that the GVL selectivity fell to only 67.6% when the reaction was carried out at 463 K for only 1 h, as compared with

80.9% for 2 h (Table 3, entries 2 and 3). One can thus infer that small amount of intermediate 4-HPE were preserved in a short reaction time under the low temperature. Moreover, the selectivity to compound **5** increased gradually with temperature; nevertheless, the total selectivity to compounds **4** and **5** did not exceeded 7%, because the vast majority of aldehyde coupled readily with ethanol to form acetal (Scheme 1).

Based on the above observations, a temperature of 513 K was chosen for the subsequent studies. The influence of reaction time was investigated as shown in Table 4. It can be seen that the EL conversion was raised significantly from 54.9% to 98.5% with the reaction time ranging from 20 to 180 min. As for GVL formation rate, however, it showed a sharp reverse trend. As a consequence, a compromise can and should be kept between the EL conversion and the GVL formation rate by regulating the reaction duration to optimize the GVL production. Based on these considerations, 60 min could be selected as a trade-off to alleviate the conflict between the conversion and the desired product formation rate. Furthermore, in accordance with the effect of reaction temperature, no significant alteration for the selectivities to GVL and E4EOPA were observed. However, the total selectivity of compounds **4** and **5** was slightly increased.

Table 5 shows that the EL conversion was increased and the GVL formation rate was decreased with increasing catalyst loading or the mass ratio of catalyst to EL. In addition, the selectivity of GVL fluctuated noticeably, and a maximum of 84.5% was obtained at the mass ratio of 1:2. The total selectivity to compounds **4** and **5** was slightly improved with an increasing catalyst loading. An EL conversion of 92.9% was observed, even when the concentration

Table 3
CTH of EL to GVL catalyzed by $\text{Zr}(\text{OH})_4$ at different temperature.^a

Entry	Tem. (K)	Conversion (%)	Selectivity (%)				GVL formation rate ($\mu\text{mol/g/min}$)
			GVL	1	4	5	
1	453	37.3	67.7	9.2	2.5	1.7	58.8
2	463	44.5	67.6	9.3	2.5	1.9	71.0
3 ^b	463	59.9	80.9	12.4	3.5	2.7	56.8
4	473	50.9	84.6	11.8	3.1	2.5	100.9
5	483	65.9	80.3	10.8	2.8	2.6	122.9
6	493	71.9	82.0	10.8	2.6	2.7	139.4
7	503	77.3	79.9	10.0	2.3	3.0	147.0
8	513	89.1	84.5	10.5	1.8	3.2	179.0
9	523	75.8	82.5	9.7	1.8	3.4	147.4
10	533	84.2	80.8	9.7	1.3	3.3	158.4

^a Reaction conditions: 2 g EL, 38 g ethanol, 1 g $\text{Zr}(\text{OH})_4$, 60 min, 500 rpm, N_2 at atmospheric conditions.

^b Reaction time: 120 min.

Table 4Effects of reaction time on the CTH of EL to GVL over $\text{Zr}(\text{OH})_4$.^a

Entry	Time (min)	Conversion (%)	Selectivity (%)				GVL formation rate ($\mu\text{mol/g/min}$)
			GVL	1	4	5	
1	20	54.9	78.2	9.1	1.6	2.2	293.9
2	40	74.5	82.1	9.9	1.5	2.8	200.4
3	60	89.1	84.5	10.5	1.8	3.2	179.0
4	80	90.0	82.5	10.0	2.2	3.6	130.8
5	100	95.9	81.5	9.9	2.0	3.9	110.8
6	180	98.5	80.1	10.2	1.8	4.3	61.6

^a Reaction conditions: 2 g EL, 38 g ethanol, 1 g $\text{Zr}(\text{OH})_4$, 513 K, 500 rpm, N_2 at atmospheric conditions.**Table 5**Effects of mass ratio of catalyst to EL on the CTH of EL to GVL over $\text{Zr}(\text{OH})_4$.^a

Entry	Mass ratio catalyst: EL	Conversion (%)	Selectivity (%)				GVL formation rate ($\mu\text{mol/g/min}$)
			GVL	1	4	5	
1	1:1	97.0	76.0	9.5	1.7	4.3	86.5
2	1:1.5	91.5	75.2	9.2	1.5	3.3	120.5
3	1:2	89.1	84.5	10.5	1.8	3.2	179.0
4	1:2.5	79.9	75.4	9.3	1.3	2.5	176.0
5	1:3	76.1	81.6	9.9	1.3	2.6	220.3
6	1:4	63.1	75.9	8.9	1.0	2.0	225.8
7 ^b	1:4	80.2	72.1	7.0	2.1	2.9	272.5
8 ^b	1:2	92.9	68.5	7.7	2.5	4.2	149.8

^a Reaction conditions: 2 g EL, 38 g ethanol, 513 K, 60 min, 500 rpm, N_2 at atmospheric conditions.^b 4 g EL as feed.

of EL was increased to 10 wt% (Table 5, entry 8). However, the GVL selectivity decreased to only 68.5%, implying more undesirable side reactions occurred.

One can conclude that the EL conversion and the GVL formation rate were highly sensitive to the reaction temperature, duration and catalyst loading. However, the selectivities to GVL and by-products were not affected noticeably by these parameters under the test conditions.

3.5. Recycling tests and characterizations of catalysts

In a typical recycling test, the catalyst was separated from the reaction mixture by filtration after reaction, and then dried at 343 K for 2 h before reuse in the next cycle. As can be seen from Fig. 1, the $\text{Zr}(\text{OH})_4$ catalyst exhibited exceptional stability and activity with

an acceptable decrease after the first cycle. Even in the tenth cycle, an EL conversion of 76.5% and a GVL yield of 65.3% were obtained.

Fig. 1 Fresh and spent catalysts were characterized to provide an insight into the stability of the catalytic materials. XRD spectrums of the fresh and the spent catalysts (Fig. 2) show similar patterns with two broad and weak peaks (amorphous form), indicating that no new phase was formed under the applied conditions. SEM images show that both the fresh and spent $\text{Zr}(\text{OH})_4$ catalysts were composed of aggregations of primary crystallites (Fig. 3). The size of aggregations (<20 nm) and surface morphology of the catalysts were apparently unchanged before and after use. These results indicate that the $\text{Zr}(\text{OH})_4$ catalyst has outstanding stability under the applied conditions, which was in line with the catalytic activity results of recycling tests.

From the FT-IR patterns (Fig. 4), one can infer that carbon residues or coke formed on the catalyst surface should be

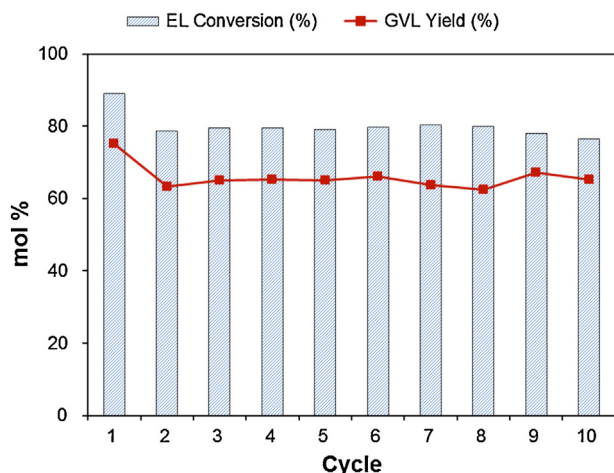


Fig. 1. Recycling of the catalysts in the CTH of EL to GVL catalyzed by $\text{Zr}(\text{OH})_4$. Reaction conditions: 2 g EL, 38 g ethanol, 513 K, 1 g catalyst, 60 min, 500 rpm.

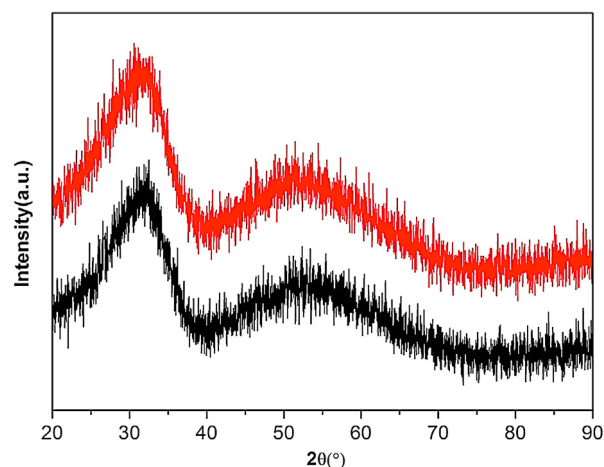


Fig. 2. XRD patterns for the fresh catalyst (black) and the spent catalyst (red) after the tenth cycle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

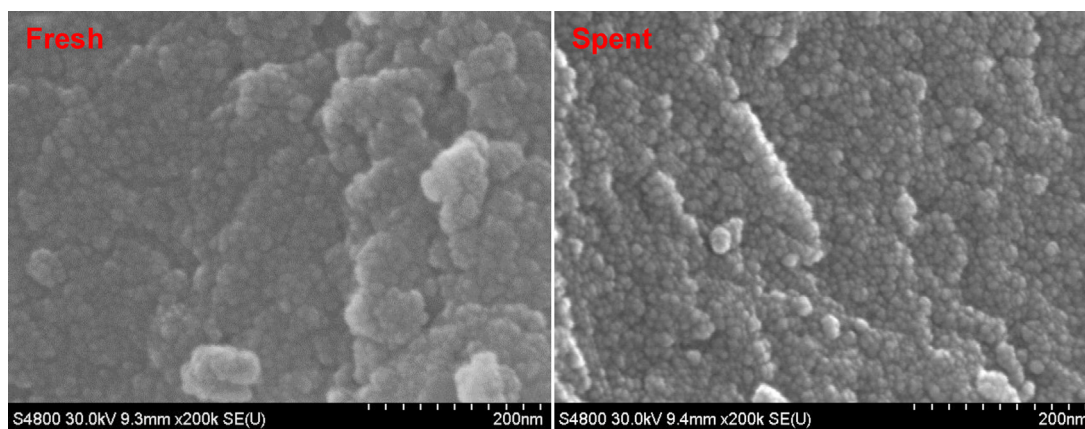


Fig. 3. SEM images for the fresh catalyst and the spent catalyst after the tenth cycle.

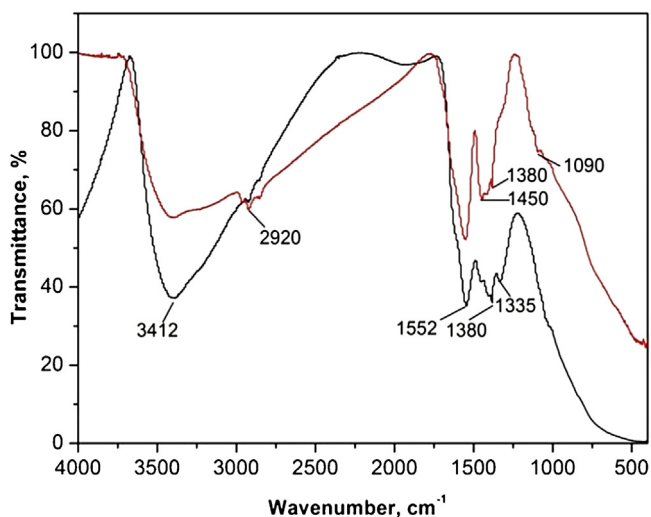


Fig. 4. FT-IR patterns for the fresh catalyst (black) and the spent catalyst (red) after the tenth cycle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

responsible for the slight deactivation of the catalyst after the first run. Compared to the fresh catalyst, new absorption peaks appeared at about 2920, 1450 and 1090 cm^{-1} , probably resulted from the above-mentioned carbon residues. For instance, the new peak at 2920 cm^{-1} is representative of the stretching vibration of C–H. In addition, the results of elemental analysis and BET surface areas for the fresh and the spent catalysts also corroborate this deduction (Table 6). Carbon residues of 4.4 wt% on the catalyst led to an acceptable drop in the specific surface area of the catalyst, which in turn resulted in the slight deactivation of the catalyst. However, only 4.6 wt% carbon residues and a slight decline in the specific surface area of the catalyst were observed even after the tenth run. No excessive carbon deposits increased with the recycling of the catalyst was the probable reason for the good catalytic activity of the catalyst after the first use.

Table 6
Elemental analyses and BET surface areas for the fresh and spent catalysts.

Recycle times	Carbon residues ^a (wt%)	S_{BET} (m^2/g)
Fresh	0.0	191.7
1	4.4	167.1
10	4.6	153.0

^a Based on the mass ratio of carbon to the catalyst solids.

As can be seen from Fig. 5, the observation of more weight loss of the fresh catalyst than the spent catalyst before 373 K indicated that the former absorbed much water than the latter owing to carbon deposits on the spent catalyst surface (Table 6). Nevertheless, the weight loss of the spent catalyst was reached 12.3 wt%, which was higher than 10.7 wt% of the fresh catalyst as the temperature increased subsequently to 1273 K. This result suggested that probable carbon residues accumulated on the catalyst surface after reaction, in accordance with the results of elemental analysis. However, the weight loss ratio of both of the fresh and the spent catalyst were below the theoretical value (22.6 wt%), implying the catalyst probably existed as $\text{ZrO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ rather than $\text{Zr}(\text{OH})_4$ [44,45]. The exothermic peaks with a continuous weight loss appeared around 704 and 756 K were attributed to the enthalpy of the transformation of the amorphous zirconia into the crystalline zirconia, accompanying by the release of hydroxyl groups of remaining Zr–OH species in the incomplete ZrO_2 lattice (Scheme S1, supplementary material) [44]. Carbon deposits were probably responsible for the delay of the crystal transition of the spent catalyst.

3.6. Poisoning tests and reaction mechanism

A series of poisoning tests were performed by introducing various additives to the reaction system to gain more insight to the

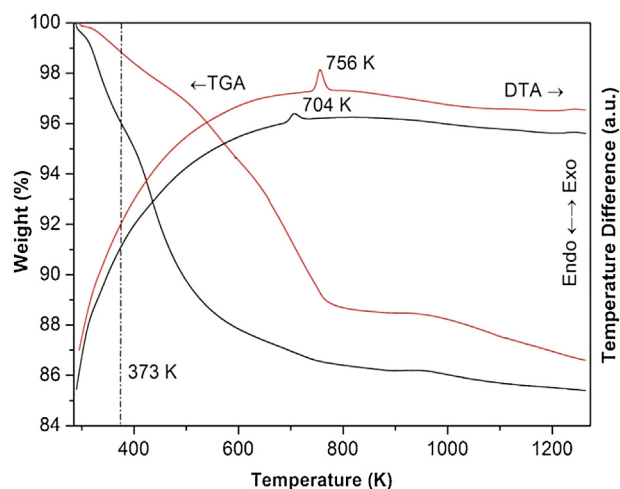


Fig. 5. TGA-DTA profiles for the fresh catalyst (black) and the spent catalyst (red) after the tenth cycle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 7
Effects of additives on the conversion of EL to GVL over $\text{Zr}(\text{OH})_4$.^a

Run	Additives	Conversion (%)	Selectivity (%)				GVL formation rate ($\mu\text{mol/g/min}$)
			GVL	1	4	5	
1	No	89.1 (1.33 wt%) ^d	84.5	10.5	1.8	3.2	179.0
2	5 wt% H_2O	89.6	81.4	8.8	1.4	1.7	171.9
3	10 wt% H_2O	92.0	80.5	7.6	0.9	0.9	173.7
4	Pyridine ^b	81.1	82.2	10.2	2.8	3.5	157.8
5	Benzoic acid ^b	23.2	78.7	8.8	0.4	2.6	42.9
6	10 bar O_2 ^c	66.9 (3.33 wt%) ^d	58.6	6.6	4.6	2.7	93.5

^a Reaction conditions: 2 g EL, 38 g ethanol, 513 K, 1 g catalyst, 60 min, 500 rpm, N_2 at atmospheric conditions.

^b 1 g additive was introduced.

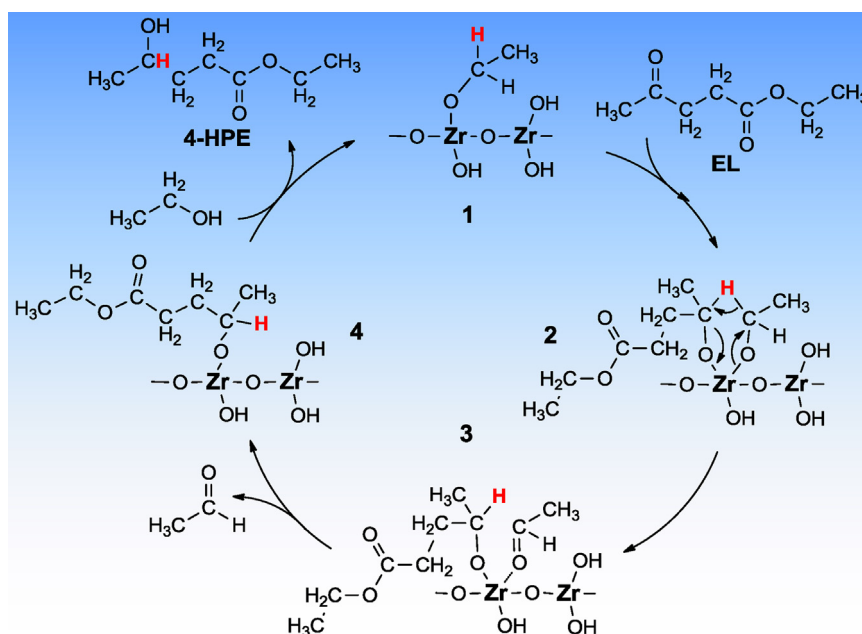
^c Pressure of O_2 was 4.5 bar after reaction.

^d Moisture content of the solution after reaction.

mechanism for the CTH of levulinate esters via MPV reduction. As can be seen from Table 7, a small amount of water slightly improved the EL conversion with a little decrease of the selectivity of by-products (Table 7, entries 2 and 3). On the basis of Le Chatelier's principle, the side reactions could be suppressed with increasing moisture because the formation of by-products involved a dehydration process. The addition of pyridine had little impact on the EL conversion and the products selectivities, whereas a sharp decline in the EL conversion was observed when benzoic acid was introduced (Table 7, entries 4 and 5). The catalyst is extremely sensitive to benzoic acid, indicating their catalytic activity for the CTH of levulinate esters was closely related to basic sites on the catalyst surface. Namely, $-\text{OH}$ probably played a vital role in the hydrogen transfer process. Small amounts of dissociative alkoxide species were probably formed by reaction with the alcohol and then catalyzed the CTH of EL. To verify the possibility that zirconium ethoxide was the active intermediate, $\text{ZrO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ catalyst was mixed with ethanol and then the mixture was heated to 473 K over 1 h under nitrogen. After the reactor cooled to room temperature, the solid catalyst was removed by filtration. Subsequently, EL was added to the filtrate and then reacted with recovered ethanol under the same conditions. No GVL was detected after reaction showing that no zirconium ethoxide was formed under these conditions. In other words, the CTH of EL was occurred on the solid catalyst surface under the prescribed reaction conditions. Although hydride

transfer is generally believed to be responsible for the MPV reduction [46]; no direct evidence was obtained to indicate the existence of H^- so far. The autoclave was filled with O_2 (10 bar) at the beginning of reaction and the water content was measured by a Karl Fischer titrator (Mettler Toledo V20) after reaction (Table 7, entry 6). It is remarkable that the oxygen pressure was dropped to 4.5 bar after reaction, and the EL conversion fell to 66.9% with 3.33 wt% water content. However, only 1.33 wt% water was measured in the absence of oxygen (Table 7, entry 1). These results imply that oxygen competed with EL to capture H^- and was reduced to water subsequently.

In light of the above mentioned observations, and in combination with the results of the characterizations for the fresh and spent catalyst, a plausible mechanism for the CTH of EL to 4-HPE via MPV reduction was proposed through a catalytic cycle involving a six member ring transition state (Scheme 2). As shown in Scheme 2, ethanol was adsorbed to the catalyst surface and dissociated to the corresponding alkoxide **1**. EL then coordinated with this alkoxide to form a six-membered ring transition state **2**. Between intermediates **2** and **3**, the hydride was free from the alkoxide and attacked to the carbonyl of EL by the concerted process of a six-membered ring-like structure. At this point the new carbonyl (aldehyde) was released and gave off the intermediate species **4**. Finally, another ethanol from solution displaced the newly reduced carbonyl (4-HPE) to regenerate the alkoxide **1**. Each step in the cycle



Scheme 2. Proposed mechanism for the CTH of EL to 4-HPE over $\text{ZrO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ using ethanol as a hydrogen donor.

was believed to be reversible and the reaction was driven by the thermodynamic properties of the intermediates and the products [47]. The newly formed 4-HPE was not stable and readily converted to GVL. As a consequence, reaction balance would greatly incline to 4-HPE in turn resulted in a high GVL yield. It should be noted that this mechanism for hydrogen transfer was also applicable equally well to using other alcohol H-donors for the reduction of EL to GVL.

4. Conclusions

We developed a simple and efficient CTH process for the production of GVL from biomass-derived EL via MPV reduction over metal hydroxides. The reaction pathway and mechanism for this CTH process were proposed. Compared with the hydrogenation catalyzed by noble-metal catalysts, this CTH strategy has three important advantages: (1) employing inexpensive metal hydroxides as catalyst, (2) employing safe and easy-to-stored alcohols as the H-donors, and (3) having a high selectivity to carbonyl without excessive reduction products. Furthermore, this CTH strategy catalyzed with metal hydroxides can also be applied to selective reduction of other aldehydes or ketones, whether derived from biomass or not.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.10.021>.

References

- [1] G. Fischer, L. Schrattenholzer, *Biomass Bioenergy* 20 (2001) 151–159.
- [2] S. Liu, *J. Bioproc. Eng. Biorefinery* 1 (2012) 129–139.
- [3] G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 106 (2006) 4044–4098.
- [4] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 107 (2007) 2411–2502.
- [5] M. Yabushita, H. Kobayashi, A. Fukuoka, *Appl. Catal., B* 145 (2013) 1–9.
- [6] J.C. Serrano-Ruiz, D.J. Braden, R.M. West, J.A. Dumesic, *Appl. Catal., B* 100 (2010) 184–189.
- [7] H. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, *Science* 316 (2007) 1597–1600.
- [8] L. Hu, G. Zhao, W. Hao, X. Tang, Y. Sun, L. Lin, S. Liu, *RSC Adv.* 2 (2012) 11184–11206.
- [9] Y. Román-Leshkov, J.N. Chheda, J.A. Dumesic, *Science* 312 (2006) 1933–1937.
- [10] S. Liu, *Bioprocess Engineering: Kinetics, Biosystems, Sustainability and Reactor Design*, Elsevier, Amsterdam, 2013.
- [11] L. Peng, L. Lin, J. Zhang, J. Zhuang, B. Zhang, Y. Gong, *Molecules* 15 (2010) 5258–5272.
- [12] J.J. Bozell, L. Moens, D.C. Elliott, Y. Wang, G.G. Neuenschwander, S.W. Fitzpatrick, R.J. Bilski, J.L. Jarnefeld, *Resour. Conserv. Recycl.* 28 (2000) 227–239.
- [13] I.T. Horváth, H. Mehdi, V. Fábos, L. Boda, L.T. Mika, *Green Chem.* 10 (2008) 238–242.
- [14] V. Fábos, G. Koczó, H. Mehdi, L. Boda, I.T. Horváth, *Energy Environ. Sci.* 2 (2009) 767–769.
- [15] D. Fegyverneki, L. Orha, G. Láng, I.T. Horváth, *Tetrahedron* 66 (2010) 1078–1081.
- [16] C.E. Chan-Thaw, M. Marelli, R. Psaro, N. Ravasio, F. Zaccheria, *RSC Adv.* 3 (2013) 1302–1306.
- [17] D.M. Alonso, J.Q. Bond, J.C. Serrano-Ruiz, J.A. Dumesic, *Green Chem.* 12 (2010) 992–999.
- [18] J.Q. Bond, D.M. Alonso, D. Wang, R.M. West, J.A. Dumesic, *Science* 327 (2010) 1110–1114.
- [19] J.P. Lange, R. Price, P.M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, *Angew. Chem. Int. Ed. Engl.* 49 (2010) 4479–4483.
- [20] Z.-Q. Duan, F. Hu, *Green Chem.* 14 (2012) 1581–1583.
- [21] E.I. Gurbuz, J.M. Gallo, D.M. Alonso, S.G. Wettstein, W.Y. Lim, J.A. Dumesic, *Angew. Chem. Int. Ed. Engl.* 52 (2013) 1270–1274.
- [22] S. Wettstein, D. Martin Alonso, Y. Chong, J. Dumesic, *Energy Environ. Sci.* 5 (2012) 8199–8203.
- [23] D.M. Alonso, J.M.R. Gallo, M.A. Mellmer, S.G. Wettstein, J.A. Dumesic, *Catal. Sci. Technol.* 3 (2013) 927–931.
- [24] W.R. Wright, R. Palkovits, *ChemSusChem* 5 (2012) 1657–1667.
- [25] D. Martin Alonso, S. Wettstein, J. Dumesic, *Green Chem.* 15 (2013) 584–595.
- [26] Z. Yan, L. Lin, S. Liu, *Energy Fuels* 23 (2009) 3853–3858.
- [27] H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L.T. Mika, I.T. Horváth, *Top. Catal.* 48 (2008) 49–54.
- [28] M. Chalid, A.A. Broekhuis, H.J. Heeres, *J. Mol. Catal. A: Chem.* 341 (2011) 14–21.
- [29] M.M. Wright, D.E. Daugaard, J.A. Satrio, R.C. Brown, *Fuel* 89 (2010) S2–S10.
- [30] C. Chang, G. Xu, X. Jiang, *Bioresour. Technol.* 121 (2012) 93–99.
- [31] L. Peng, L. Lin, H. Li, *Ind. Crops Prod.* 40 (2012) 136–144.
- [32] L. Peng, L. Lin, H. Li, Q. Yang, *Appl. Energy* 88 (2011) 4590–4596.
- [33] R. Mao, Q. Zhao, G. Dima, D. Petraccone, *Catal. Lett.* 141 (2010) 271–276.
- [34] A.M. Hengne, C.V. Rode, *Green Chem.* 14 (2012) 1064–1072.
- [35] X.-L. Du, Q.-Y. Bi, Y.-M. Liu, Y. Cao, K.-N. Fan, *ChemSusChem* 4 (2011) 1838–1843.
- [36] Z. Yang, Y.-B. Huang, Q. Guo, Y. Fu, *Chem. Commun.* 49 (2013) 5328–5330.
- [37] C.F. de Graauw, J.A. Peters, H. van Bekkum, J. Huskens, *Synthesis* 10 (1994) 1007–1017.
- [38] J.R. Ruiz, C. Jiménez-Sanchidrián, *Curr. Org. Chem.* 11 (2007) 1113–1125.
- [39] J.R. Ruiz, C. Jiménez-Sanchidrián, J.M. Hidalgo, J.M. Marinas, *J. Mol. Catal. A: Chem.* 246 (2006) 190–194.
- [40] M. Chia, J.A. Dumesic, *Chem. Commun.* 47 (2011) 12233–12235.
- [41] X. Tang, L. Hu, Y. Sun, G. Zhao, W. Hao, L. Lin, *RSC Adv.* 3 (2013) 10277–10284.
- [42] J.C. van der Waal, P.J. Kunkeler, K. Tan, H. van Bekkum, *J. Catal.* 173 (1998) 74–83.
- [43] M.G. Al-Shaal, W.R.H. Wright, R. Palkovits, *Green Chem.* 14 (2012) 1260–1263.
- [44] P. Manivasakan, V. Rajendran, P. Ranjan Rauta, B. Bandhu Sahu, B. Krushna Panda, *J. Am. Ceram. Soc.* 94 (2011) 1410–1420.
- [45] C. Huang, Z. Tang, Z. Zhang, *J. Am. Ceram. Soc.* 84 (2001) 1637–1638.
- [46] V.A. Ivanov, J. Bachelier, F. Audry, J.C. Lavalley, *J. Mol. Catal.* 91 (1994) 45–59.
- [47] R. Cohen, C.R. Graves, S.T. Nguyen, J.M.L. Martin, M.A. Ratner, *J. Am. Chem. Soc.* 126 (2004) 14796–14803.